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## CELLULAR CELLULOSIC MATERIAL CONTAINING A BIOCIDE AGENT AND PROCESS FOR PREPARING SAME

The present invention relates to a cellular cellulosic material containing a biocide agent and to a process for producing same.

This invention covers the field of sponges, spongecloths, foamed sponges and similar products for use in 10 domestic cleaning and maintenance works or personal hygiene, and proposes an improvement in the resistance of said products against attacks from micro-organisms.

According to the invention, the protecting agent (or biocide(s)) is introduced at some stage in the process for 15 producing the cellulosic product, in the form of matrix particles; the matrix in said particles having a double function which is:

to protect the active agent when this is introduced into the cellulosic product during the production 20 process and during the final phases of production (and to protect the preparation medium from said active agent);

to control the active agent releasing speed during use of the product.

Various methods have already been proposed in the prior art, for protecting cellulosic products or domestic cleaning tools against attacks from micro-organisms, and among these:

the introduction, during the production of the prod- 30 uct, of a biocide agent in the reactive mixture. This method, which is described, for example, in patent U.S. Pat. No. 4 476 251, is especially adapted to synthetic foams such as polyurethane foams, obtained by crosslinking of a mixture of different 35 polymers. On the other hand, it cannot be adapted to the production of cellular cellulosic products insofar as the active agent, which is not protected, would then be irreparably affected or lost during the cellulose regeneration step, which step is espe- 40 cially aggressive. The process for producing said cellular cellulose products, known as viscose process, and described in particular in patent FR-A-812 502 includes the steps of preparing a paste-like mass notably from a cellulosic solution, such as 45 rials according to the invention. viscose, from fibrous materials, pigments and expanding agents; shaping such a mass in particular by molding or by coating on either side or on one side of a grid or by deposition on a conveyor belt; heating same optionally in an adequate medium so 50 that the action of the expanding agents is exerted, and the cellulose is regenerated. This last step is a particularly aggressive one. It can be performed either by passing an a.c. current between electrodes in contact with the pulp, or by placing the pulp in 55 contact with an acid medium (of pH near 0), at temperatures around 70° C. for a few minutes (socalled acid regeneration for making sponge-cloths), or by placing said pulp in contact with a basic medium (of pH near 12), at temperatures around 60 100° C. for a few hours (so-called basic regeneration for making sponges). Whatever the embodiment used, said step in the process for producing cellular cellulosic products excludes the introduction of the unprotected active agent;

the introduction, during the production of the product, of a polymer adapted to fix a biocide agent, said biocide agent being itself introduced at the end of the production process. Said method, which is particularly described in patent application WO 85/02422, is adapted to the products in regenerated cellulose. Nevertheless, with said method, the ac-

tive agent has to be iodine, which for example, implies a coloring which is incompatible with the currently proposed application:

the introduction, after the production of the cellulosic product, of a biocide agent. Said agent is fixed in the cellulose network, either by precipitation—as illustrated in patent U.S. Pat. No. 3,018,192, FR-A-1 200 663 and FR-A-1 345 614—or by a latex—as illustrated in patents U.S. Pat. No. 2,257,911—or by a technique combining precipitation and binding-as illustrated in application EP-A-0 358 572-. The different variants of said method are adapted to the cellular cellulosic products. However, they impose, for those which are based on precipitation, the use of biocides liable to have an ionic charge, and for all of them, posttreatments which may be expensive;

the introduction of an active agent or of a system for controlling the release of an active agent between the different parts constituting the final product: in a cavity—as illustrated in application EP-A-0 314 340 —at the level of an adhesive seal—as illustrated in application EP-A-0 500 460-. This method is only applicable to combined :products and to pads. It will also be noted that, it is difficult, with the method described in application EP-A-0 314 340. to ensure a release of the active ingredient which is adapted to the needs, seeing that said active ingredient is released under the pressure applied by the

An original method is currently proposed, also for the purpose of protecting cellular cellulosic materials against micro-organisms.

The cellular cellulosic materials according to the invention contain in their cellulose network, particles of matrix type which contain at least one biocide agent and which are capable, in the presence of moisture or water, to controllable release said biocide agent or agents.

Characteristically, microparticles, trapped in the cellulose network, are found in the cellular cellulosic mate-

Said microparticles are of matrix type and not of the reservoir type; They contain at least one biocide within a matrix.

The first function of said matrix is to protect said biocide or biocides during the incorporation of the microparticles into the cellular cellulosic material being produced, and during the final production phases of said material. Said microparticles have to be introduced before the cellulose regeneration phase in order to be distributed out into, the cellulose network of the finished product.

The second function of said matrix is to allow, while in contact with moisture or water, a controlled release of said biocide or biocides. Such release is controlled and programmed as regards the quantity of biocide released in time. Such quantity is optimized in order to ensure the protection of the cellular cellulosic material from micro-organisms throughout its period of use.

Said matrix must be capable of both withstanding severe physico-chemical conditions (cellulose regeneration conditions, during which the cellulose xanthate solution (viscose) is converted into non-soluble cellulose: severe conditions such as defined above), and re-